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Trace Elements Associated with Oil Shale and Its Processing

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United States
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Agency Region 8
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MAY 1977

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ASSOCIATED WITH OIL SHALE
AND ITS PROCESSING

Prepared For

Industrial Environmental Research Laboratory

(Cincinnati)

Environmental Protection Agency

Cincinnati, Ohio 45268

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TRACE ELEMENTS ASSOCIATED WITH OIL SHALE AND ITS PROCESSING

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1.0 INTRODUCTION AND SUMMARY

All fossil fuels contain minor elements which may potentially be mobilized during extraction, processing, and end use. Certain coals and petroleum oils for instance are known to contain relatively large amounts of cadmium, boron, selenium or vanadium. Such elements may be released to the environment as processing wastes or combustion emissions and can have toxic effects on plants, animals, and man. The processing of fossil fuels may also involve the use of catalysts and other chemicals which contain large amounts of metalic elements (e.g., Co, Ni or Mo in petroleum refining catalysts).

Because of the potential substitution of oil shale products for coal and petroleum products, and because of the large volumes of oil shale which would have to be extracted and/or processed in order to provide such substitutes, concern has developed regarding the mobilization and fate of trace elements contained in oil shale. This concern has resulted in the generation of a body of data regarding the composition of raw oil shale, oil shale products, and processing wastes. Studies have also been conducted to determine the potential for release of trace elements to the air, water, and biological environments.

This report includes a summary of existing trace element composition data for shale and its products, an evaluation of these data and related studies to estimate the distribution of trace elements among shale products during oil shale processing, and predictions of the disposition and ultimate fate of trace elements after waste disposal or product use. Although some uncertainties and data gaps exist at present, a number of general conclusions have been deduced from the available trace element data and studies.

- For many elements, wide ranges of concentrations have been reported for oil shale and its products. These ranges reflect natural geographic and verticle profile variations in the shale, differences in retorting methods, and uncertainties associated with various sampling and analytical techniques.

- Compared to average rocks, oil shale contains much higher levels of Se and As, moderately higher levels of Mo, Hg, Sb, and B and lower levels of Co, Ni, Cr, Zr and Mn. Other elements are present in concentrations typical of common rocks.
- Most elements are not converted to volatile or oil soluble substances during retorting and are consequently retained by processed shale. However, up to 30% of Hg, 15% of As, and 8% of Se in raw shale can be found in shale oil, retort gases and retort waters.
- Shale oils contain trace elements derrived from raw shale in both soluble and particulate form. The concentrations of most trace elements in shale oil are similar to or less than those found in many petroleum oils. Arsenic is a notable exception, with levels in shale oil up to 50 ppm compared to a maximum of about 4 ppm for residual fuel oil.
- Retort gases contain very small amounts of metallic and heavy elements. Particulate and H_2S control equipment will likely collect most of the trace elements before release to the atmosphere.
- Levels of most trace elements in retort waters are in the parts per billion range. Many treated municipal and industrial wastewaters contain higher levels of transition and heavy metals than do retort waters. Arsenic, boron, and floride may present problems for direct discharge to surface waters or for irrigation use.
- Most metals contained in retorted shale are not readily water soluble. However, elements which form anionic species (B, F, Mo, Se) can be leached from retorted shales by percolating water. Properly compacted processed shale has a low permeability, and only small amounts of leachate are expected under field conditions in the Piceance and Uinta Basins.

- The effects of using retort water and/or process wastewater for moisturizing retorted shale are not well known. The available data suggest that the additional amounts of soluble trace elements added to retorted shale in wastewaters are small. Further, the alkaline and absorbtive properties of retorted shale are expected to immobilize most metallic elements.

- Vegetation growing on retorted shale may accumulate toxic levels of boron. Molybdenum may accumulate in some plant species to levels toxic to grazing animals.

- Measurements during combustion tests in a utility boiler suggest that large fractions of several elements in crude shale oil are unaccounted for in flue gas particulate matter. Elements such as Hg, Se, and As may exit the stack in gaseous form. Less volatile elements are likely retained in ash or deposits within the boiler system.

- During upgrading and refining of crude shale oil, metallic elements tend to concentrate in higher boiling fractions and in shale coke. Volatile elements (e.g., As and Se) found in lower boiling distillates would be removed prior to or during catalytic hydrogenation. Spent catalyst media containing Ni, Co, Mo and shale derived arsenic and other trace elements would be either disposed with retorted shale or shipped for reprocessing.

2.0 THE ELEMENTAL COMPOSITION OF OIL SHALE AND ITS PRODUCTS

Oil shale is generally defined as organic rich sedimentary rock which yields substantial quantities of liquid hydrocarbons when subjected to destructive distillation. Oil shales of the Green River formation of Colorado, Utah, and Wyoming are actually dolomitic marlstones rather than true "shales" since they contain little or no clay. Like true shales, however, oil shales have a laminated structure and natural cleavage planes.

2.1 KEROGEN

The organic component of oil shale ranges from 5 to 30% by weight and consists mostly of kerogen, a heteroatomic, wax-like polymer which is insoluble in organic solvents. Around 10% of the organic material is bitumen (also a polymer, but soluble in organic solvents). Cross-linking of the polymer units within the shale matrix is extensive and accounts for the cohesive nature of rich shales. Oxygen, sulfur, and nitrogen occur primarily as heterocyclic and polymeric cross-linking components of the kerogen molecule. Table 1 presents the major element composition of organic material in oil shale.

2.2 MAJOR INORGANIC COMPONENTS OF GREEN RIVER SHALE

The inorganic fraction of Mahogany oil shale consists mainly of silicon, calcium and magnesium, with smaller amounts of iron, aluminum, sodium and potassium. Table 1 presents selected composition data for the inorganic fraction of oil shales. Elements are commonly reported as oxides with no implication as to mineralological form.

Table 2 summarizes the results of several mineralogical studies of oil shales. The inorganic fraction of raw oil shales consists mainly of quartz, dolomite, calcite, albite, and potassium feldspar. Dawsonite, nathcolite, analcine, and siderite are also present in some shale samples. Generally, the silicate minerals (quartz, felspar, albite) tend to be associated with the organic layers in laminated oil shales; dolomite and calcite are dominant in the inorganic layers.

2.3 TRACE ELEMENTS IN OIL SHALE

In recent years, considerable data on the minor element composition of oil shales have accumulated. Figures 1, 2, and 3 show the ranges of values reported by the U.S.G.S., the LERC, and the lessees of Tracts C-a and C-b for selected trace element of particular environmental interest. For many of the selected elements, reported levels vary by one order of magnitude and for a few elements, two orders of magnitude. The ranges reflect at least three factors; 1) natural variations in oil shale samples in a vertical profile depending on mineral and organic matter composition, 2) natural geographic variations, and 3) variations in measurements due to different sampling, preparation, and analytical techniques. In most cases, it is difficult to distinguish the relative importance of these three factors. For example, variations between laboratories for shale from the same area are often as great as variations geographically as determined by the same laboratory. In addition, values for some elements are consistently higher (e.g., Ni and Cr) or lower (e.g., Pb) according to LERC data than according to U.S.G.S. data (Figures 1 & 2). One possible explanation for anomalously high Ni and Cr levels is sample contamination from stainless steels during crushing and screening.

Where similar sample preparation and analytical techniques have been employed, some geographic and vertical distribution trends have been preliminarily identified. For instance, shale from Tract C-a appears to be generally higher in Cd and lower in Se, As, and F than shale from Tract C-b (Figure 3). In contrast, the U.S.G.S. data for Mahogany Zone shales from the Piceance and Uinta Basin do not indicate significant geographic differences in levels of most elements. LERC data suggest that typical levels of Cd and Sb may be higher, and levels of Ni and Cr lower in the saline zone oil shale of the northern Piceance Basin than in Mahogany Zone shale (Table 3-a).

Table 1. Major Element Composition of Raw Green River Oil Shales

	Mahogany Zone in Colorado			Mahogany Utah	R4 Zone Colorado
	(1)*	(2)	(3)	(4)	(5)
ORGANIC FRACTION (~14%)			Percent of Total Organic Material		
C	-	-	80.5	80.7	-
H	-	-	10.3	10.4	-
N	-	-	2.4	2.56	-
S (organic)**	-	-	1.04	1.0	-
O	-	-	5.8	5.33	-
			100	100	
INORGANIC FRACTION (~86%)			Ash Composition (Percent of Raw Shale Basis)		
SiO_2	27.8	26	26 - 40	30.1	27 - 41
CaO	15.1	17.5	8.3 - 17.5	15.4	3 - 7.5
Al_2O_3	8.5	6.5	6.3 - 9.4	6.7	7 - 10
MgO	6.5	5.3	4.5 - 5.6	7.0	1 - 2.7
Fe_2O_3	3.0	2.6	2.6 - 4.3	-	3 - 4
Na_2O	2.0	2.6	1.8 - 2.7	1.5	1 - 2.5
K_2O	1.5	1.0	1.0 - 3.4	1.8	1.3 - 2.6
P_2O_5	-	0.9	-	-	2 - 0.6
SO_3**(inorganic)	1.8	0.5-4.4	0.1 - 1.2	1.5	3.4 - 6
Mineral CO_2	19.9	-	9.9 - 25.7	22.4	-
TOTAL	86.2	-	80.4	86.4	-

*See References at end of text.
**Sulfur in shale is approximately 33% organically bound and 67% inorganically combined; the latter mainly as Pyrite and Marcasite (FeS_2).

Table 2. Major Mineral Components of Green River Oil Shales

Mineral	Chemical Formula	Mahogany Zone						R4 Zone	R5 & R4 Zones	
		Order of Abundance*		Wt % Raw Shale				Order of Abundance*	Wt % Raw Shale	
		(2)**	(5)	(3)	(6)	(4)	(7)	(2)	(8)	(9)
Dolomite	$CaMg(CO_3)_2$	1	1	33	48	32	32	2	20	24
Calcite	$CaCO_3$	4	2	20		16	14	3	N/A	
Albite	$NaAlSi_3O_8$	3	5	12	N/A	10	10	4	10	10
Illite	$KAl_2(AlSi_3)O_8(OH)_2$	N/A	6	11	13	19	12	N/A	Trace	N/A
Quartz	SiO_2	2	4	10	13	15	13	1	20	15
Analcite	$NaAlSi_2O_6\ H_2O$	5	3	7	4	1	N/A	3	N/A	N/A
Feldspar	$KAlSi_3O_8$	N/A	7	4	21	6	6	5	5	10
Pyrite	FeS_2	7	8	2	1	N/A	1	8	N/A	N/A
Nahcolite	$NaHCO_3$	N/A	N/A	0	0	1	N/A	6	N/A	17
Dawsonite	$NaAl(OH)_2CO_3$	6	N/A	0	0	N/A	N/A	7	12	9.5

* 1 > 2 > 3 etc.

**See references at end of text

N/A = not available

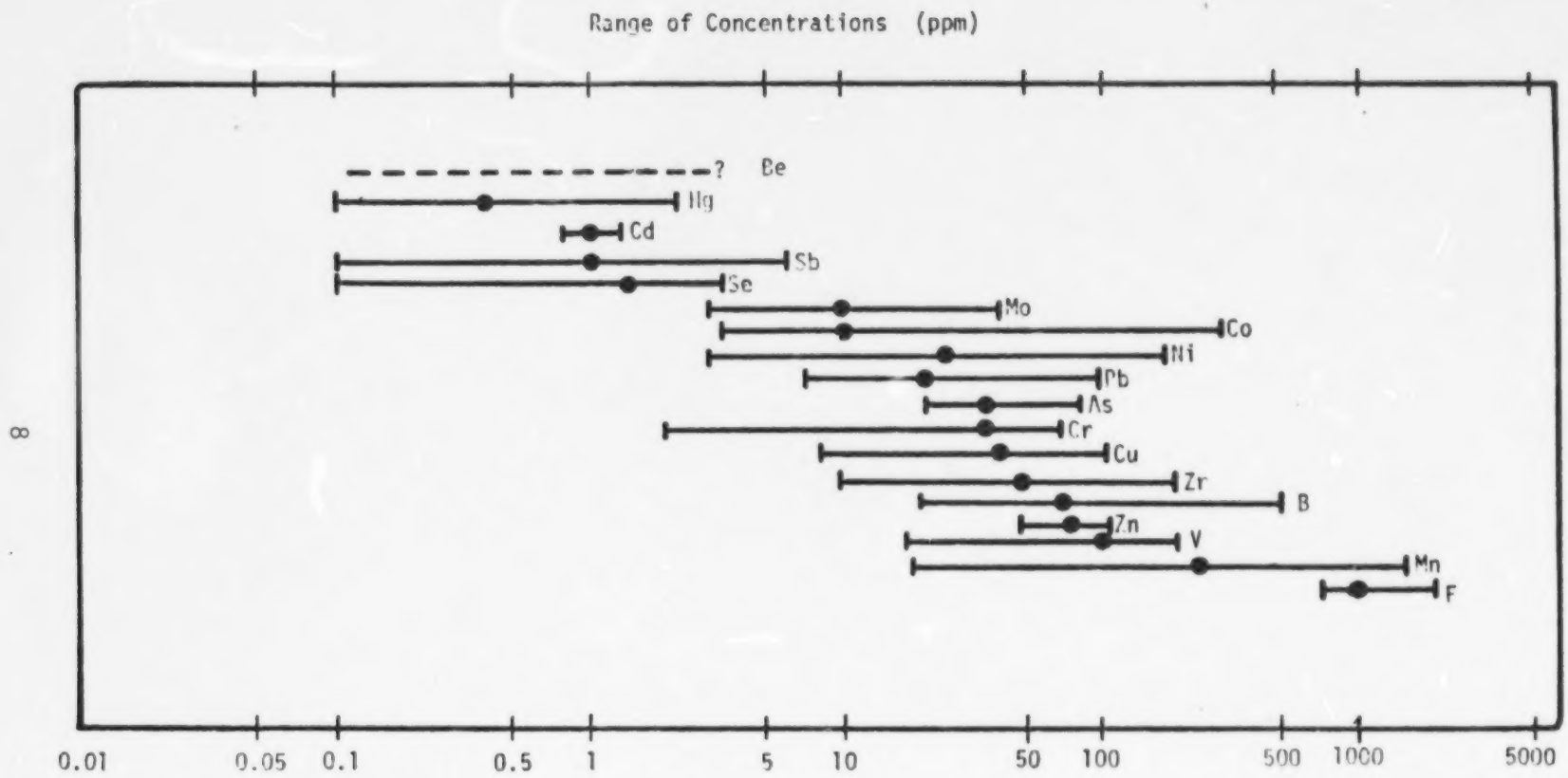

Figure 1. Levels of Selected Elements in Raw Oil Shale - U.S. Geological Survey (2,10)

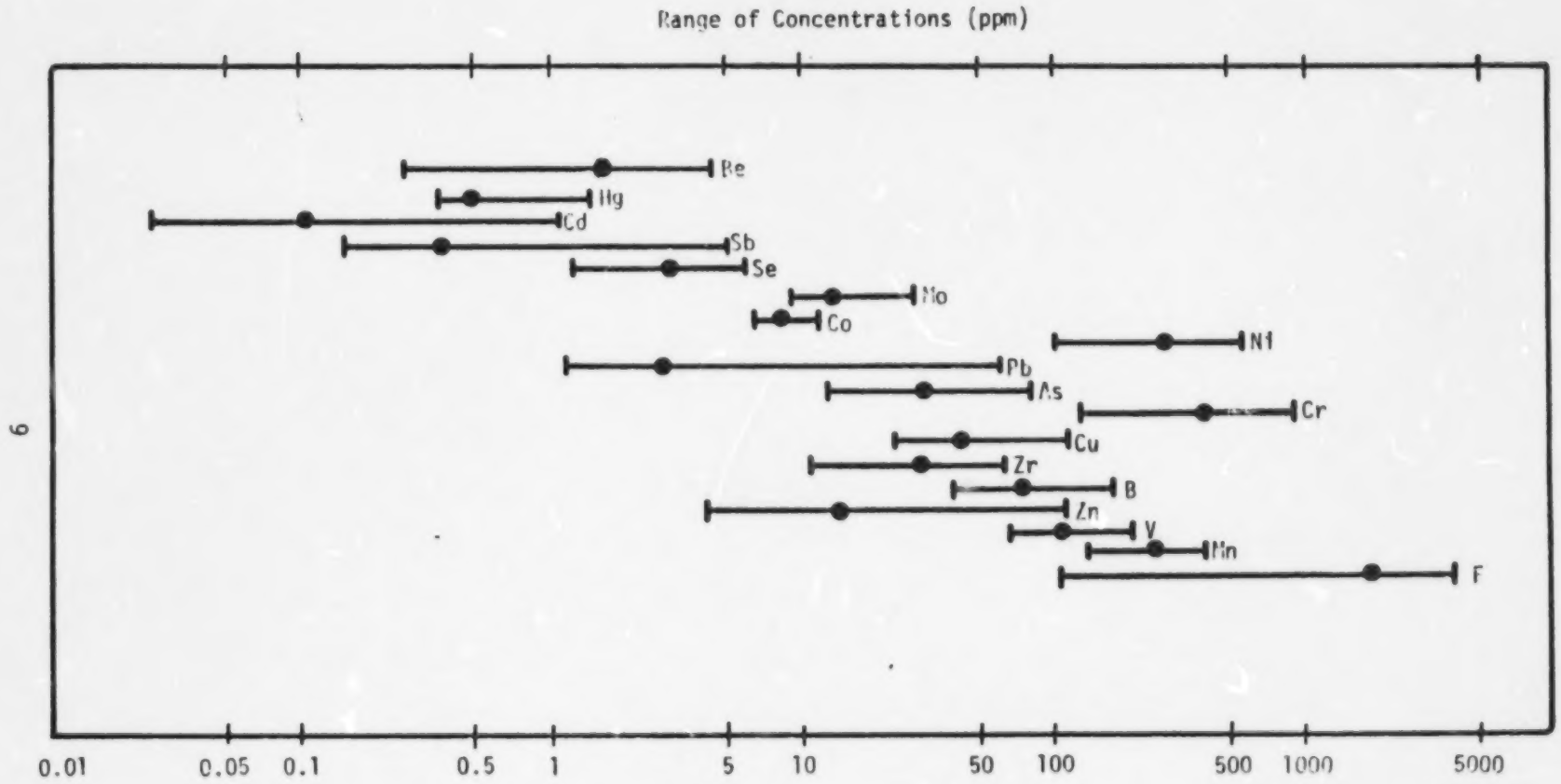

Figure 2. Levels of Selected Trace Elements in Raw Oil Shale - LERC (11)

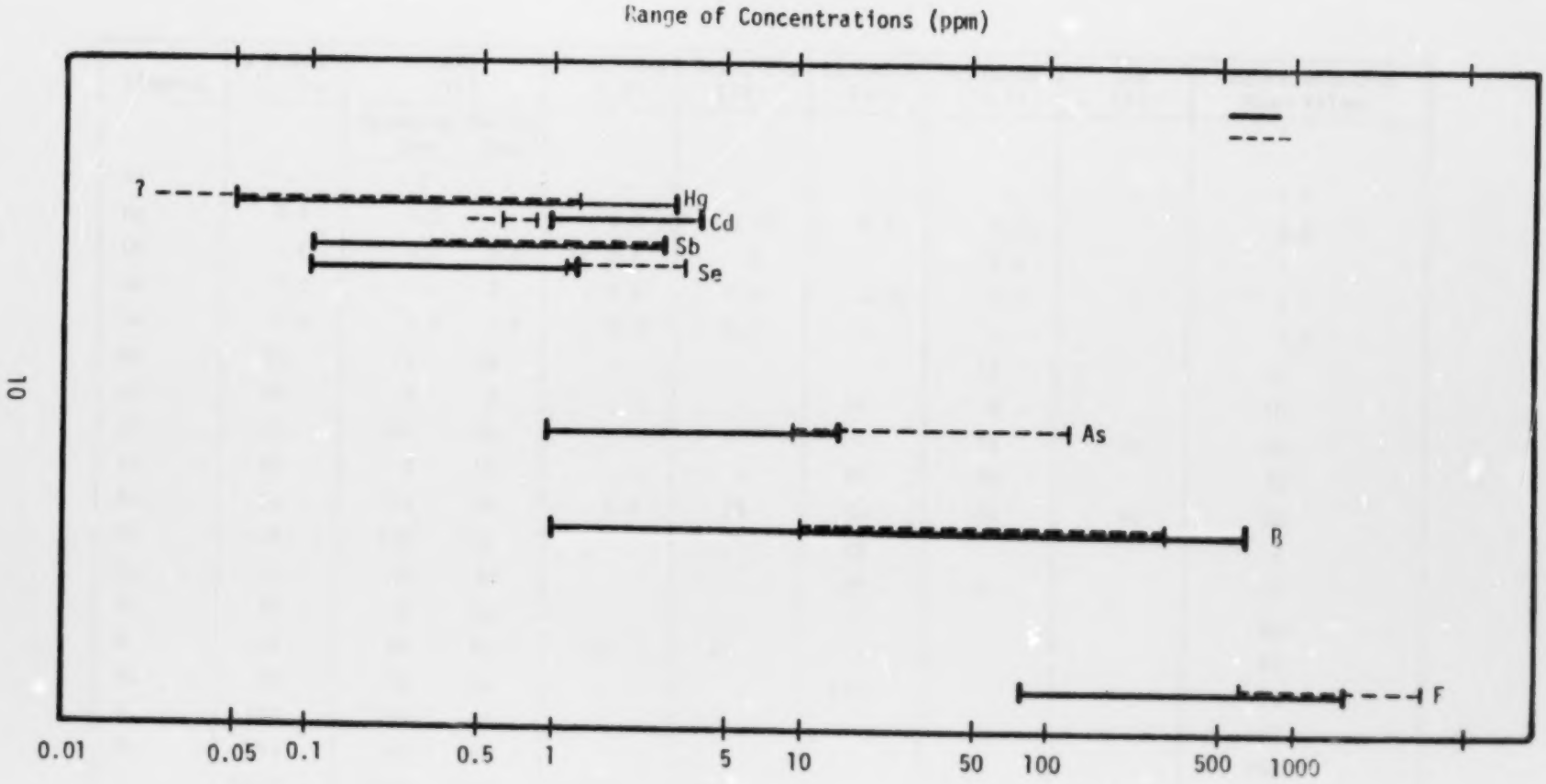

Figure 3. Levels of Selected Trace Elements in Raw Oil Shale on Federal Lease Tracts C-a and C-b (12,13)

Table 3-A. Mean Levels of Selected Trace Elements in Raw Oil Shale - Comparison of Reported Data for Class I Elements* (ppm)

Element	U.S.G.S. (1,10)	LERC (11)		Tract C-a (12)	Tract C-b (13)	Battelle (14)	Berkeley (15,16)	TRW (17)	Representative Mean Value
		Mahogany Zone	Saline Zone						
Be	-	2	1	-	-	-	-	-	1.3
Hg	0.4	0.5	-	0.6	0.22	0.2	0.13		0.4
Cd	1.0	0.1	0.4	2.4	.5	-	1.0		1
Sb	1.0	0.4	3	0.5	1.2	0.35	1.5	1	1
Se	1.5	3.0	1.5	0.32	2.2	5	-		1.5
Mo	10	15	30	-	-	-	14		10
Co	10	9	4			11	9		10
Ni	25	300	85			30	16	20	25
Pb	20	3	15	-	-	40	30		20
As	35	30	20	6.5	38	80	88	44	35
Cr	34	400	100			25	-		34
Cu	37	45	30			64	37		37
Zr	44	30	50			-			40
B	65	80	50	129	41	-			65
Zn	70	15	30			115			70
V	100	100	80			-	-		100
Mn	250	250	250						250
F	1000	2000	1000	550	1300				1000

*Class I Elements - Those which potentially pose environmental hazards and/or tend to be relatively abundant in fossil fuels.

Table 3-B. Summary of Analytical Techniques Used for Trace Elements in Oil Shale

Element	U.S.G.S. (1,10)	LERC (11)	C-a (12)	C-b (13)	Batelle* (14)	Berkeley* (15)	TRW (17)
Be	-	SSMS	-	-	-	-	
Hg	Wet Ash,F.A.A.	NAA	Wet Ash, FAA		NAA	IZAA	
Cd	Ash, A.A.	SSMS	Ash, A.A.		-	IZAA	
Sb	Wet Ash,Spec.	SSMS	Wet Ash, A.A.		NAA	NAA	Wet Ash, Spec.
Se	Wet Ash, X.R.F.	SSMS	Wet Ash, Fluorometry		XRF	-	
Mo	Ash, E.S.	SSMS			-	NAA	
Co	Ash, E.S.	SSMS			NAA	NAA	
Ni	Ash, E.S.	SSMS/XRF			NAA/XRF	NAA	Wet Ash, Spec.
Pb	Ash, A.A.	SSMS/XRF			NAA/XRF	IZAA	
As	Wet Ash, Spec.	SSMS/NAA	Wet Ash, A.A.		NAA/XRF	NAA	Wet Ash, Spec.
Cr	Ash, E.S.	SSMS/XRF			NAA	NAA	
Cu	Ash, A.A.	SSMS			NAA/XRF		
Zr	Ash, E.S.	SSMS					
B	Ash, E.S.	SSMS/XRF	Ash, Spec.				
Zn	Ash, A.A.	SSMS/XRF			XRF		
V	Ash, E.S.	SSMS/XRF					
Mn	Ash, A.A.	SSMS/XRF					
F	Wet Ash,S.I.E.	SSMS	Wet Ash, S.I.E.				

Symbols

A.A. = Atomic-absorption spectroscopy
E.S. = Optical emission spectroscopy
F.A.A. = Flameless atomic absorption spectroscopy
Spec. = Spectophotometric
S.I.E. = Specific ion electrode
XRF = X-ray fluorescence
SSMS = Spark source mass spectrometry
NAA = Neutron activation analysis
IZAA = Isotope Zeeman atomic absorption spectroscopy

*SSMS,NAA,& XRF analyses were performed on raw shale powder.

Despite the ranges and uncertainties in the data, approximate or representative levels for most minor elements can be estimated. Tables 3-A and 4 list mean values for two groups of minor elements, respectively, as reported by or consolidated from several sources. The elements in the first class (Table 3-A) were selected for major consideration because of (1) potential environmental hazards which they may pose (2) their relative abundance in conventional fossil fuels (e.g., coal) and associated processing or waste streams. Elements in the second class (Table 4) generally pose less of a hazard and/or are less abundant in fossil fuels. For the elements in class 1, a summary of analytical techniques employed by the various laboratories is presented in Table 3-B.

The approximate mean levels for minor elements shown in Table 3-A and 4 have little meaning without a comparison with other geologic materials and an identification of individual chemical forms or mineralogical residences. In Table 5, mean levels of Group 1 elements in oil shale are compared to mean levels in Piceance Basin soils and to average crustal abundances. Similar levels for many elements in oil shale and Piceance Basin soil is not surprising since these soils were derived from oil shale and/or associated rocks. However, Hg, Se, Mo, As, and F appear to be present in larger amounts in shale. Compared to average rocks of the earth's crust, oil shale is enriched in Hg, Cd, Sb, Se, Mo, As, and B, and slightly depleted in Co, Ni, Cr, Zr, and Mn (enrichment factors of .5 to 1.5 are considered within the normal range of normal variation). For Class II elements (Table 4), only Li, Cs, and Tl appear to be enriched to any degree in oil shale compared to common rocks. Only three elements (Se, As, and V) are thought to exist at least in part as components of kerogen in oil shale; the remainder exist as inorganic trace minerals (e.g., zircon) or as substitute elements in major minerals (e.g., pyrite).

The enrichment of oil shale in certain elements is consistent with data for other sedimentary rocks containing organic material (e.g., coal). Elements such as Mo, B, Zn, Cu, Se, are essential in small quantities for metabolic activities in living plants and/or animals, and are therefore expected to have been present in the parent organic debris from which the sedimentary rocks were derived. Other elements such as Hg, Cd, and As, U, and V can form stable

organic compounds or complexes, or can participate in ion exchange reactions with organic material and become entrapped in the matrix of organic sediments. After sediment deposition, entrapped elements may be altered chemically to form inorganic compounds. Elements such as Cu, Zn, Ni, and Co may also be enriched in sediments by precipitation as sulfides from groundwater which contacts reducing organic material after deposition.

Table 4. Mean Levels of Selected Trace Elements in Raw Oil Shale - Comparison of Reported Data for Class II Elements* (ppm)

Element	U.S.G.S. (1,10)	LERC (11)	DRI (18)	Battelle (14)	Berkeley (15)	Representative Mean Value	Average Crustal Abundance(19)	Enrichment Factor
Tl	1500	3600		-	-	2000	5700	0.4
Sc	7	6	16	6	6	7	22	0.3
Li	70	15	80	-	-	70	20	3.5
Rb	-	110	100	67	88	100	90	1.1
Cs	-	0.2	6	5	7	6	3	2.0
Ba	350	650	220	350	540	350	425	0.8
Sr	300	900	800	400	-	500	375	1.3
Y	10	20	25	-	-	20	33	0.6
Nb	-	6	7	-	-	6	20	0.3
Hf to Au	-	1	-	1	-	1	1	-
Tl	-	1	-	-	-	1	.5	2.0
Ga	10	10	10	7	-	10	15	0.7
Ge	-	2	0.6	-	-	1	1.5	0.7
Sn	-	3	1	-		1	1	1.0
Te	-	.5		-		.5	.5	-
Cl	-	160		-		160	130	1.2
Br	-	1	0.4	-		0.6	2.5	0.2
I	-	1	0.1	-		0.5	0.5	1.0
La to Lu	-	230	150	120		150	150	1.0
Th + U	12	5	10	10	17	10	12	0.8

*Class II Elements - Those which generally pose less of a potential environmental hazard than Class I elements and/or do not tend to be relatively abundant in fossil fuels.

Table 5. Mineralogical Residence and Relative Abundance of Selected Trace Elements in Oil Shale (ppm)

Element	Mineralogical Residence in Oil Shale (2)	Representative Mean Level in Raw Shale	Average Crustal Abundance (19)	Enrichment Factor	Average for Soils in Piceance Cr. Basin (20)	Enrichment Factor
Be	Unknown	1.5	2.8	0.5	2.4	0.6
Hg	Unknown	0.4	0.8	5	.04	10
Cd	CdS	1	0.2	5	-	-
Sb	Unknown	1	0.2	5	0.9	1.1
Se	Substitute for S in Pyrite & Organic Matter	1.5	0.05	30	0.3	5
Mo	Possibly sulfides	10	1.5	7	5	2
Co	Substitute for Fe in Pyrite	10	25	0.4	8	.8
Ni	NiS	25	75	0.3	21	1.1
Pb	PbS or Fe Substitute in Pyrite	20	13	1.6	25	0.8
As	Substitute for S in Pyrite,Organic Matter	35	1.8	19	6	6
Cr	Substitute for Fe in Pyrite	34	100	0.3	60	0.6
Cu	Substitute for Fe in Pyrite	37	55	0.7	30	1.2
Zr	Zircon	40	165	0.3	270	0.2
B	Potassium Feldspar	65	10	7	61	1.0
Zn	ZnS (sphalerite)	70	70	1.0	80	0.9
V	Organic Matter	100	135	0.7	56	1.8
Mn	Substitute for Fe in Ferroan Dolomite,Siderite,Magnesio-siderite	250	950	0.3	490	0.5
F	Fluoride, cryolite	1000	625	1.6	500	2

2.4 LEVELS OF TRACE ELEMENTS IN PROCESSED OIL SHALE

Retorting of oil shale is generally effected by heating the rock to temperatures of 800° - 1000°F. Some minor elements in oil shale can form volatile or oil soluble compounds at these temperatures and thus can appear in shale oil, retort gases or retort waters. Most elements however, are not volatile at retorting temperatues and are not converted into mobile forms by the retorting process. Table 6 is a compilation of minor element composition data for processed oil shale as determined by several laboratories. The data in Table 6 are mean levels and do not reveal the considerable ranges of values from which the averages for individual laboratories were derived The variations between laboratories reflect shale origin, analytical techniques, and method of retorting. Within the limitations of the data, however, only the elements Hg and Se appear to be depleted in processed shales compared to raw shales by 70% or more. Cd, Sb, As, and Be and Zn appear to be depleted by 30% or more.

The depletion factors in Table 6 must be taken only as a rough indication of element mobility in oil shale, since several elements (e.g., Co, Ni, Pb, Cr, and B) are calculated to be more abundant in processed shale than in raw shale. More reliable estimation of minor element retention or release by shale during processing requires measurement of the same shale before and after processing using equivalent analytical techniques. Even with such measurements, limits of analytical precision, non-representativeness of samples, and sample contamination from retorting or sample preparation equipment can obscure trends in the data.

2.5 LEVELS OF TRACE ELEMENTS IN SHALE OILS

Minor elements in crude shale oils may be present in organic compounds or complexes (e.g., As in arsines) or may be part of suspended shale fines (either raw or retorted). Table 7 summarizes the available minor element data in crude shale oils. As is the case with the data for raw and processed shales, considerable variations occur between laboratories and individual shale oils. Elements other than C, H, N, S, and O constitute a total of about 200-300 ppm in a typical shale oil.

Table 6. Mean Levels of Trace Elements in Processed Oil Shale (Calculated as ppm raw shale basis*)

Element	Ash, Mahogany Zone Utah (4)	Ash, Mahogany Zone Colo.(21)	Paraho Direct Mode Retorted Shale(18)	Paraho Indirect Mode Retorted Shale(18)	Fischer Assay Retorted Shale(22)	TOSCO II Retorted Shale(36)	Gas Combustion Retorted Shale(14)	Gas Combustion Retorted Shale(15)	Representative Mean Value	Representative Value for Raw Shale	Depletion Factor
Be	-	35	2	0.7					1	1.5	0.7
Hg	-	0.1	0.07	.03	0.38		.002	.04	.04	0.4	0.1
Cd	-	0.14	-	-	2.1			0.56	0.5	1	0.5
Sb	-	0.39	0.7	0.8	0.3		2.7		0.5	1	0.5
Se	-	0.08	0.3	0.2	0.4	4.9	2.9		0.3	1.5	0.2
Mo	-	4.9	12	10		38		7	10	10	1.0
Co	-	39	13	16			17	8	16	10	1.6
Ni	70	11	38	14		38	56	19	38	25	1.5
Pb	100	10	18	11		42	80	34	34	20	1.7
As	-	7.2	21	18	4.1	105	73	58	25	35	0.7
Cr	170	49	136	66			42	244	100	34	2.9
Cu	-	15	44	26		62			26	37	0.7
Zr	33	9.3	43	62			106		43	40	1.0
B	136	140	52	18	87				100	65	1.5
Zn	35	13	16	21		108	100		35	70	0.5
V	78	29	116	88					80	100	0.8
Mn	420	34	600	272				270	250	1.0	
F	-	1700	1000	450	380				900	1000	0.9

*Where ash equivalent of raw shale is not known a value of 0.8 is assumed for calculations in this table.

Table 7. Levels of Minor Elements in Shale Oils (ppm)

Class I Elements	Gas Combustion Shale Oil LERC(11)	Gas Combustion Shale Oil Battelle(14)	Gas Combustion Shale Oil Paraho(23)	Gas Combustion Shale Oil USBM(24)	Gas Combustion Shale Oil, Berkeley(15)	Gas Combustion Shale Oil, Paraho(25)	Gas Combustion Shale Oil Paraho(26)	TOSCO II Shale Oil(27)	Fischer Assay Shale Oil(36)	Paraho Indirect Mode Shale Oil(27)	Representative Level In Shale Oil
Be	-	-	.02								.02
Hg	0.2	.65	.16		.09-3.5						0.3
Cd	0.11	-	.2		.01						0.1
Sb	0.02	.008	.54				0.5			.5	.02
Se	0.2	.86	.08						0.2		.4
Mo	5-14	-	-								2
Co	.8-7	.37	-								1
Ni	2-55		2.4	6.4		2.5-2.9		6	1.1		5
Pb	0.4	90	.54		.02				7.8		.5
As	.5-53	5	10			20-22	22-65	40	24-29	35-65	20
Cr	.2	.04	1.2						< 1		.2
Cu	.1-1.5	-	-								.5
Zr	0.1	-	-								.1
B	3	-	7								5
Zn	3	2.7	.075								2
V	1		5	6.0		0.33-.37	< 3-30	3		60	3
Mn	0.1		4								1
F	.1-3		-								1
Other Elements											
Fe	8-390	30	-	108		33-71		100	6		60
Ti	1		36								15
Al	.1-19		36								15
Ba	.1	.01	21								2
Mg	.4-100		14								7
Ca	.5-39		12								7
Na	-	19	-								19
Si	110		-								20

Table 8. Approximate Percentages of Shale Derived Minor Elements Which Appear in Crude Shale Oil

Class I Elements	Representative Level in Shale Oil (ppm)	Quantity in Shale Oil per Ton Raw Shale (10^{-6} lbs/ton)	Quantity in Representative Raw Shale (10^{-6} lbs/ton)	Percent of Element Contained in Raw Shale Appearing in Shale Oil
Be	0.02	4	4000	0.1
Hg	0.3	60	800	7.5
Cd	0.1	20	2000	1
Sb	0.02	4	2000	8
Se	.4	80	3000	3
Mo	2	400	20000	2
Co	1	200	20000	1
Ni	5	1000	50000	2
Pb	.5	100	40000	.25
As	20	4000	70000	6
Cr	.2	40	70000	.06
Cu	.5	100	70000	.1
Zr	.1	20	90000	.02
B	5	1000	130000	0.8
Zn	2	400	140000	.3
V	3	600	200000	.3
Mn	1	200	500000	.04
F	1	200	200000	.01
Other Elements		(10^{-6} lbs/ton)	(lbs/ton)	%
Fe	60	12000	40	.03
Ti	15	3000	2	.15
Al	15	3000	60	.005
Ba	2	400	0.8	.05
Mg	7	1400	80	.002
Ca	7	1400	280	.0005
Na	19	3800	20	.02
Si	20	4000	300	.001

Table 9. Comparison of Trace Element Levels in Shale Oil, Crude Oils, and Residual Fuel Oil (ppm)

Element	Representative Shale Oil	Petroleum Crude Oils (28)				Residual Fuel Oil #6 (29)
		California	Libya	Venezuela	Alberta	
Be	.02					.0005 - .5
Hg	0.3	23	-	0.03	0.08	.002 - 0.4
Cd	0.1					.003 - 1
Sb	.02	0.056	.055	0.30	-	.003 - .5
Se	.4	0.36	1.1	0.37	.009	.02 - 0.15
Mo	2			7.9		
Co	1	13	.032	0.18	.003	
Ni	5	98	49	117	0.61	20 - 90
Pb	0.5					1 - 4
As	20	0.66	0.08	0.28	.002	0.2 - 1
Cr	.2	0.64	0.002	0.43	-	0.7 - 4
Cu	.5	.93	.2	.2	-	0.2 - 1
Zr	.1					-
B	5					.002 - 0.2
Zn	2	9.8	63	0.69	0.67	.4 - 2
V	3	7.5	8.2	1100	0.7	40 - 113
Mn	1	1.2	0.8	0.2	0.05	0.2 - 1
F	1					.004
Fe	60	69	4.9	4.8	0.7	10 - 20
Ti	15					-
Al	15					-
Ba	2					0.3 - 5
Mg	7					2 - 3
Ca	7	13	13	20	3	.4 - 30
Na	19					8 - 30
Si	20					

A comparison of the representative quantities of minor elements in shale oil to those of raw oil shale is shown in Table 8. More than 5% of Hg, Sb, and As and more than 1% of Cd, Se, Mo, Co. and Ni, originally present in raw shale can be accounted for in crude shale oil. In contrast, less than 0.001% of major raw shale elements Ca, Mg and Si are found in crude shale oil. These data suggest that most of the Class I elements in shale oil are not simply associated with suspended shale fines, but rather exist as either organic complexes or as suspended insoluble minerals whose composition differs from that of raw or retorted shale.

Although most Class I elements are enriched in shale oil relative to the parent shale, their absolute levels in shale oil are in the same range as or lower than those found in conventional petroleum crude and residual oils (Table 9). A noteworthy exception is arsenic, which is found in significantly higher concentrations in shale oils than petroleum oils(boron and fluoride also appear to be present at higher levels, although the available data base is limited).

2.6 TRACE ELEMENTS IN RETORT GASES

The minor elements in oil shale may potentially be present in retort gas gases in particulate or gaseous form. Raw or retorted shale particulate matter may be suspended or entrained in retort gases, and such material would be expected to have compositions similar to those discussed previously. Some elements (e.g., Hg and As) can form volatile compounds at retorting temperatures and may appear as either vaporous components of retort gases or as particulate matter resulting from condensation of volatile substances during cooling of the gas. Table 10 presents selected trace element analyses of LERC simulated in-situ retort gas. Gaseous components are artificially defined as those not retained by a 0.5u nucleopore filter and do not necessarily indicate gaseous components. As calculated in the table, a very small fraction of As, Hg, Fe, Cs, and Zn original in the shale appear in raw retort gases.

Table 10. Levels of Minor Elements in Off-Gas From LERC Ten Ton Retort (14)

Element	Form	Concentration in Off-Gas (µg/SCM)	Amount of Element in Raw Shale (grams/ton)	Amount of Element in Retort Gas (mg/ton)	Percent of Element Found in Retort Gas
Arsenic	Gas **	15			
	Particulate	0.4			
		15.4	32	7.5	0.02
Mercury	Gas	2.2			
	Particulate	0.15			
		2.35	.36	1.2	0.33
Iron	Gas	120			
	Particulate	6			
		126	18,000	63	0.00035
Chromium	Gas	90			
	Particulate	2			
		92	34	46	0.14
Zinc	Gas	40			
	Particulate	0.5			
		40.5	64	20	0.03

* Assumes net gas production of 500 SCM/ton shale, Ref.(30).
**Gaseous forms are defined as those not collected by a 0.5u neopore filter.

Table 11. Levels of Minor Elements in Retort Waters (ppm) Compared to Levels in Selected Municipal Effluents and to Water Standards

Element	Gas Combustion Simulated In-Situ Retorts					Indirect Heated Retorts		Federal Drinking Water Standards(33)	Municipal/ Industrial Final Effluent JWPCP(34)	Municipal Final Effluent Oxnard(34)	Model Wastewater Ordinance Pretreatment Standards (35)
	LERC(31)	LERC(11)	LERC(14)	LERC(15,16)	LLL*(15,16)	TOSCO II(32)	Paraho I.D.M.*(26)				
Be	-	-	-				-				
Hg	.01	< .01	.39	.01	.02	-	-	.002	.001	.0015	.01
Cd	-		-	.001	.003	-	-	.010	.036	.017	0.2
Sb	.007	.007	.016			-	-	-	-		
Se	.005	.01	.98			.096	0.7	.01	< .01		
Mo	.47	.1	-			.006	0.1	-			
Co	.37	.07	.65			.005	< .04	-			
Ni	.26	1	-			.03	.2	-	.28	.23	1.0
Pb	.01	.1	-	.03	0.1	< .002	.2	.05	.25	.07	1.0
As	.26	6	6	2	0.3	1.0	1	.05	< .01	.007	0.1
Cr	.012	.02	< .02	-	-	.007	.3	.05	0.8	.044	0.5
Cu	.003	.007	-	.2	5	.16	.2	-	0.4	.073	2.0
Zr	.02	.07	-			.003	-	-			
B	.26	6	-			.44	5	-	1.0		
Zn	.04	.4	.43	5	1	.045	.4	5	1.45	.21	3.0
Li	-	.3	-			.006	1	-			
V	1.2	.07	-			.002	.03	-			
Mn	.023	.1	-			.019	.3	-	0.13	0.12	
F	-	25	-			.3	7	1.4-2.4			
Ba	.03	.05	.13			.09	2	1.0			
Fe	.49	25	<1			5.7	5	-	10	0.5	

* I.D.M. = Indirect Mode, LLL = Lawrence Livermore Laboratory

2.7 TRACE ELEMENT COMPOSITION OF RETORT WATER

Small quantities of shale derived elements are found in water which condenses from retort gases or which separates from shale oil. Reported levels in retort waters vary widely between retorting processes, laboratories, and input shales. Generally, most elements are present at levels below 1 ppm in retort waters although Zn, As, V, F, Ba, and Fe have been measured at higher levels. Table 11 summarizes some of the available data for waters produced by simulated in-situ and by inert gas retorting processes. Minor elements may be present as soluble inorganic salts, inorganic complexes, organometallic compounds, and as insoluble suspended particulate matter. For most elements, the chemical form in retort waters is unknown, although limited data suggest that 50% or more of Hg, As, and Zn is particulate in nature (16).

Also listed in Table 11 are the levels 1) defined by Federal drinking water standards, 2) found in the average final effluent from two California wastewater treatment facilities, and 3) defined by model pretreatment standards. Typical retort water would not meet the federal drinking water standards, but would comply with a model pretreatment ordinance for industrial wastewater, and compares favorably for many elements with the quality of the treated effluent quality from a large metropolitan wastewater treatment facility. However, retort waters may contain larger amounts of Hg, As, B, and F than the example wastewater. Although the calculations are not shown in Table 11, the total quantities for individual elements in retort waters amount to less than 1% of the quantities found in average oil shale.

3.0 TRACE ELEMENT MASS BALANCES AROUND OIL SHALE RETORTS

In the previous sections, several calculations have been performed to estimate the fraction of selected elements which appear in the various oil shale products after retorting. These calculations are crude at best, since the average values used do not necessarily represent individual products derived from individual shales. Further, differences between laboratories and analytical methods limit applicability of the mass balance approach to "average" data. In part to avoid these problems, several investigators have attempted to obtain trace element data under more controlled conditions so that mass balance estimates can be performed with greater certainty. This section is a review and summary

of recent work aimed specifically at estimating the mass balance of certain minor elements around oil shale retorting processes.

3.1 ARSENIC

The U.S. Geological Survey retorted composite Mahogany Zone oil shale (~30 - 35 gal/ton) by the standard Fischer technique and submitted the raw and retorted shale samples to a commercial laboratory for analyses of arsenic (2). The mean value (10 samples) for raw shale was 63 ppm, the retorted shale 65 ppm (Table 12). Since the retorted shale represented 84% of the weight of the raw shale, an average of 15% of the total arsenic was apparently converted to volatile or oil soluble substances during pyrolysis. Analyses of other Fischer Assay products for arsenic were not performed.

The Oil Shale Corporation (TOSCO) has reported arsenic levels in shale oil produced by the TOSCO II retorting process. Table 13 summarizes the arsenic content of this oil and its fractions (27). Because of the similar pyrolysis conditions employed in the Fischer Assay and TOSCO II processes, the oils produced by these processes should be similar in composition.

One ton of 35 gal/ton oil shale would yield a TOSCO II oil containing .009 lbs of arsenic. U.S.G.S. data indicate that the raw shale contains about 0.13 lbs of arsenic. Thus the shale oil contains about 7% of the total arsenic originally present in the oil shale, a figure which agrees well with the 6% calculated in Table 8 using averaged data for oil shales for various shale oils. The quantity of arsenic in shale oil is somewhat lower than the U.S.G.S. data would sugest assuming oil and retorted shale are the major residences for the element, although there is a large uncertainty (15% ± 9% in Table 12) in the data.

Recently the Lawrence Berkeley Laboratory (16) has constructed mass balances for several minor elements around the LERC and LLL simulated in-situ retorts. Table 14 summarizes the calculated distribution of six elements (including As) among oil shale products. These data indicate that about 1% of the arsenic originally present in raw oil shale appears in product oil in the gas combustion method of retorting. In contrast, arsenic mass balance data in Table 15 for the Fischer Assay retorting process shows 6% of the arsenic is found in that shale oil. The relatively low arsenic levels in LERC and LLL shale oils (3-7 ppm) compared to the Fischer Assay Oil (~26 ppm) are not readily explained by the differing methods of retorting. For instance, both Paraho Oil

Table 15. Distribution of Selected Trace Elements in Shale Products During Fischer Assay Retorting (36)

Element	Percent of Element from Raw Shale Which Appears in Product			
	Raw Oil Shale	Retorted Shale	Crude Shale Oil	Retort Water
Se	100	90	0.7	1.9
Ni	100	91	0.8	.3
Pb	100	96	4.1	N/A
As	100	94	5.9	.07
Cu	100	107	-	.007
Zn	100	87	6.5	.01

Table 12. Arsenic Analyses of Raw and Fischer Assay Retorted Shale Samples (2)

	Concentration in ppm			
	Raw Oil Shale (10 Samples	Retorted Shale (10 Samples)	Retorted Shale (Raw Basis)	Difference
Mean Standard	62.5	64.5	77.1	14.6
Standard Deviation	7.5	4.4	5.2	9.1
Range	55-75	60-70	72-84	-

Table 13. Arsenic Levels in TOSCO II Shale Oil Fractions (27)

Boiling Range		Volume Fraction	Arsenic Content
°F	°C	%	ppm
IBP - 400°	IBP - 200°	18	10
400°- 900°	200°- 480°	58	52
900° +	480°+	24	38
Whole Shale Oil		100	41

Table 14. Distribution of Trace Elements in Oil Shale Products During Simulated In-Situ Retorting (16,14)

Element	Retort	Percent of Element from Raw Shale Which Appears in Product					Imbalance in The Data*
		Raw Shale	Retorted Shale (16)	Crude Shale Oil (Wet) (16)	Whole Retort Water (16)	Wet Product Gas (14)	
Hg	LERC	100	21	7	.7	0.33	-72
	LLL	100	16	26	0.5		-57
Cd	LERC	100	109	.1	.01	N/A	+ 9
	LLL		89	0.3	0.01		-12
Pb	LERC	100	112	< .02	< .002	N/A	+12
	LLL		117	0.7	.01		+17
As	LERC	100	85	0.7	0.06	.02	-14
	LLL		110	1.5	0.4		+11
Cu	LERC	100	105	.07	.007		+ 5
	LLL		100	2.0	4.0		+ 6
Zn	LERC	100	112	< .02	< .002	.03	+12
	LLL		117	0.7	.01		+17

*Imbalance is the percent gain (+) or loss (-) in oil shale products compared to raw shale.

Direct Mode (gas combustion) and Paraho Indirect Mode (inert gas) contain about the same levels (20-30 ppm).

Despite the unexplained differences in mass balance estimates, two major conclusions can be drawn from the data: (1) 85 to 98% of the As in raw shale is accounted for in retorted shale, and (2) As levels in crude shale oil (3-40 ppm) are significantly higher than levels commonly encountered in petroleum crude oils.

3.2 MERCURY

Mercury is known to form a variety of relatively volatile compounds under combustion and pyrolysis conditions. A summary of several material balance estimates for mercury around gas combustion retorts is shown in Table 14. Retorted shale contains about 16-20% of the mercury input in raw shale; shale oil contains 7-26% of input; retort water less than 1%. The Berkeley investigators (16) postulated that the remaining mercury leaves the retort as a component of product gases. Averaged data in Tables 6, 8, and 11 are consistent with the Berkeley distribution of Hg among retorted shale, shale oil and retort water. However, other investigators have reported very low levels of Hg in retort gases (14). The apparent loss of Hg during retorting is not satisfactorily explained by the existing data. Analytical bias (e.g., loss of Hg during oil analyses), contamination from manometers, and/or Hg adsorption by walls of a retort are possible explanations for the mass imbalance.

3.3 ZINC, LEAD, AND COPPER BALANCES

The data in Tables 14 and 15 indicate that essentially all of the Zn, Pb, and Cu found in raw oil shale can be accounted for in retorted shale within analytical uncertainties. Average data in Tables 3-A and 6 substantiate this finding. The small amounts of these elements in shale oil are in the same range or lower than those found in petroleum "crudes."

3.4 CADMIUM, SELENIUM, AND ANTIMONY BALANCES

Based on the data in Table 6, Cd, Se, and Sb, are depleted in retorted shale compared to raw oil shale. The Berkeley data for cadmium in Table 14, however, do not indicate such depletion for that element. The calculations in Table 8 indicate that Cd, Se, and Sb in shale oil account for 1, 8, and 3 percent respectively of the amounts in raw shale. It appears that Cd generally does not form volatile or oil soluble substances under retorting

conditions, while selenium and, to a lesser extent, antimony do. These findings are consistent with expected similarities in chemical properties between Cd and Zn, Se and S, and between Sb and As.

3.5 OTHER ELEMENTS (Be, Mo, Co, Ni, Cr, Zr, V, Mn and F)

Mass balance studies have generally not been conducted for the above elements. Available composition data for oil shale and its products are not sufficient to accurately define the distribution of these elements. For some elements (e.g., Be, Zr, Mo) the quantity of data are limited. For other elements (e.g., B and F) the wide range of reported values in shale and its products precludes accurate mass balance calculations. With these limitations in mind, it appears that the elements above reside mainly in retorted shales, and are not enriched in shale oils, retort gases, or retort waters (Tables 6, 8, 10, and 11).

4.0 THE DISPOSITION AND ULTIMATE FATE OF TRACE ELEMENTS CONTAINED IN OIL SHALE PRODUCTS AND PROCESSING WASTES

In the previous sections, reported levels of minor elements in oil shale and its products have been reviewed. This section is a discussion of the expected disposition of these elements during commercial processing, end use, and/or disposal of retort gases, shale oil, retort water, retorted shale, shale oil coke, and non-shale products and wastes. In addition, the mobility, chemical forms, and biological availability of some of the trace elements in the above products and waste streams are predicted. For the purposes here, retorting technologies are broadly classified as 1) gas combustion methods (e.g., Paraho Direct Mode and Modified In-Situ), Indirect Heating methods (e.g., TOSCO II and Paraho Indirect Mode).

4.1 RETORT GASES

Retort gases from gas combustion processes may be directly burned or treated for sulfur removal prior to burning. As indicated by the limited data in Table 10, the quantities of measured elements in gas combustion retort gases are small. If the gases are directly burned, trace elements will be emitted to the atmosphere primarily as particulate matter. If the gases are to be treated for sulfur removal (e.g., by the Stretford Process) upgresam particulate removal may be required to protect scrubber solution from degredation. Baghouses or Venturi scrubbers would be expected to remove 95-99.9% of the total suspended particulate matter. The elements in Table 10 may be less efficiently collected than bulk particulate, since some (e.g., Hg) exist primarily as gases or as particulates less than 0.5u in size. Particulates not collected prior to sulfur removal are likely to be subsequently collected in scrubbing solutions used in processes such as Stretford. Trace elements collected by particulate or sulfur removal processes will become part or solid or aqueous wastes requiring disposal.

In the TOSCO II process (or similar indirect heating methods), hydrocarbon gases may be used for hydrogen production rather than as fuel. In this case, trace elements in retort gases may be removed during aqueous or

oil scrubbing of the gases, or be physically trapped or chemically reacted with catylist materials used for trace sulfur removal, water gas shifting, or methanation. The scrubbing solutions and ultimately the catalysts will require regeneration or disposal. Flue gases from the preheat system of the TOSCO II retort will also contain trace elements, although primarily in the form of raw or retorted shale particulate matter. Such particulates would be collected by high energy Venturi scrubbers and would constitute a solid waste.

4.2 RETORT WATER

The data in Table 11 summarize trace element levels found in retort waters from simulated in-situ and indirect heated retorts. Although the quantities and forms of wastewaters requiring disposal depend on the retorting process and the nature and extent of in-plant treatment and/or re-use, the trace element levels in the table are somewhat indicative of those which would be found in final plant wastewaters. Disposal of treated process wastewaters would be accomplished by one or more of the following techniques; 1) direct discharge to surface waters, 2) ponding and evaporation, 3) underground injection, and 4) moisturizing retorted shale.

The first method is generally not planned by oil shale developers, although retort waters could likely represent an acceptable effluent from a trace elements standpoint (see comparisons with other effluents and water quality standards in Table 11). The second method will tend to concentrate non-volatile substances in the pond(s), resulting in high levels of some elements in the remaining water. Precipitation of less soluble forms of some elements may decrease water concentrations at the expense of accumulation in sediments. The third method, like discharge to surface waters, may be acceptable from a trace elements standpoint, depending on the containment provided by the accepting rock formation and/or the water quality of existing aquifers. Ground water quality will be discussed later in connection with retorted shale disposal.

Finally, retort waters or process wastewaters may be used to moisturize retorted shale. In this case trace elements contained in the wastewaters would become components of a retorted shale disposal pile where their mobility should be restricted. In principle, the alkaline nature of retorted shale would tend to physically and chemically immobilize most metalic elements. The mobility of elements such as Mo, F, B, As, and Se which can form water soluble anionic species could be minimized by proper compaction to create an impermeable bed and by minimizing infiltration of surface moisture into beds. Since moisturizing of processed shale is the most commonly proposed method of wastewater disposal, the affect of adding trace elements to retorted shale in wastewater form will be further addressed in the next section.

4.3 RETORTED SHALE

Trace elements in retorted shale can be mobilized in several ways. During transport and after surface disposal winds can suspend or entrain fine particulate matter in the local atmosphere. Runoff from retorted shale disposal piles can carry suspended sediment consisting of retorted shale and shale/soil mixtures. Trace elements may also be transported by runoff as dissolved constituents (e.g., Mo, F, B). Surface mositure and ground water can infiltrate a shale bed, dissolving certain trace inorganic constituents. Finally, vegetation growing on retorted shale may extract certain trace elements from the bed, concentrate them in living tissues, and pass them on to herbavors which ingest the vegetation.

4.3.1 Fugitive Dust

The potential for atmospheric transport of trace elements in retorted shale is essentially unknown at present. With the possible exception of mercury, most trace elements do not form known substances which are volatile at ambient temperatures. Thus trace elements would tend to be found in the atmosphere primarily as components of raw and retorted shale particulate matter. It is possible that certain elements may preferentially reside in specific size fractions of retorted shales and thus be selectively favored or disfavored for transport. Without specific data to indicate otherwise, retorted shale particulate matter is expected to have the approximate composition shown earlier in Table 6. Compared to trace element levels in

particulate matter from "average" soils, only Se and As levels are likely to be significantly higher in the retorted shale particulates (see Tables 5 & 6).

4.3.2 The Water Solubility of Minor Elements in Retorted Shale

Experiments which have measured trace elements dissolved by water contacting retorted oil shales fall into three general categories: (1) laboratory "blender" experiments (2) laboratory column leaching experiments, (3) field runoff and leaching tests. Data from several "bender" experiments are summarized in Table 16 for selected elements. These data indicate that Se, Mo, B, and F are present in retorted shale in partially water soluble forms, while Cd, As, Cr, Cu, Zn, and Fe are essentially insoluble. With the exception of As, the latter elements are generally insoluble in aqueous alkaline environments, since they form insoluble hydroxides, oxides, or sulfides. The former elements however, can form water soluble anionic species under alkaline conditions (e.g., $SeO_4^=$, $Mo_4^=$, BO_3^{-3}, F^-).

The limited data bases used to construct Table 16 is not sufficient to establish major differences in the water solubility of trace elements between retorted shales produced by gas combustion and indirect heating methods. The more alkaline nature of gas combustion shales would suggest that most metals would be present in less soluble forms. On the other hand, the carbonaceous residue associated with shales retorted by indirect heating methods may physically inhibit contact and dissolution of substances from the shale.

Laboratory column experiments more closely simulate conditions of water contact which would occur in a retorted shale disposal pile than do "blender" experiments. Figure 4 depicts the concentration of five elements in the leachates from columns of TOSCO II retorted shale as a function of water volume which has passed through the column. The total quantities of F, B, Mo, As, and Se which are leached from TOSCO II shale in these column experiments after 15 pore volumes have passed is approximately the same as the quantities shown in Table 16. A distinct feature which is apparent from the column experiments is that fluorine (as fluoride) is slowly leachable from

Table 16. Quantities of Minor Elements in Retorted Shale Which Are Water Soluble According to Blender Experiments (ppm Retorted Shale Basis)

Element	Raw Oil Shale (31,38)	TOSCO II Retorted Shale(38)	Inert Gas Retorted Shale(37)	Gas Combustion Retorted Shale(37)	LERC Simulated In-Situ Retorted Shale(31)	LLL Simulated In-Situ Retorted Shale(15)	Representative Level in Retorted Shale (from Table 6)*	Percent of element in Retorted Shale Which is Water Soluble
Cd						.004	0.5	0.8
Se		.05					0.3	17
Mo	2	8	< .05	0.14			10	2-80
Pb			.14	< .05		.003	34	.01-.4
As		0.1					25	.4
Cr			< .05	1.3			100	.05-1
Cu						.010	26	.04
B	0.4-7	12			1.0		100	1-12
Zn			.02	0.12			35	.05-.3
F	3-60	80			20		900	2-9
Fe			.005	.03			20,000	< .001

*Data in Table 6 are calculated on a raw shale basis; for the accuracy intended here, the data are not recalculated on a retorted shale basis.

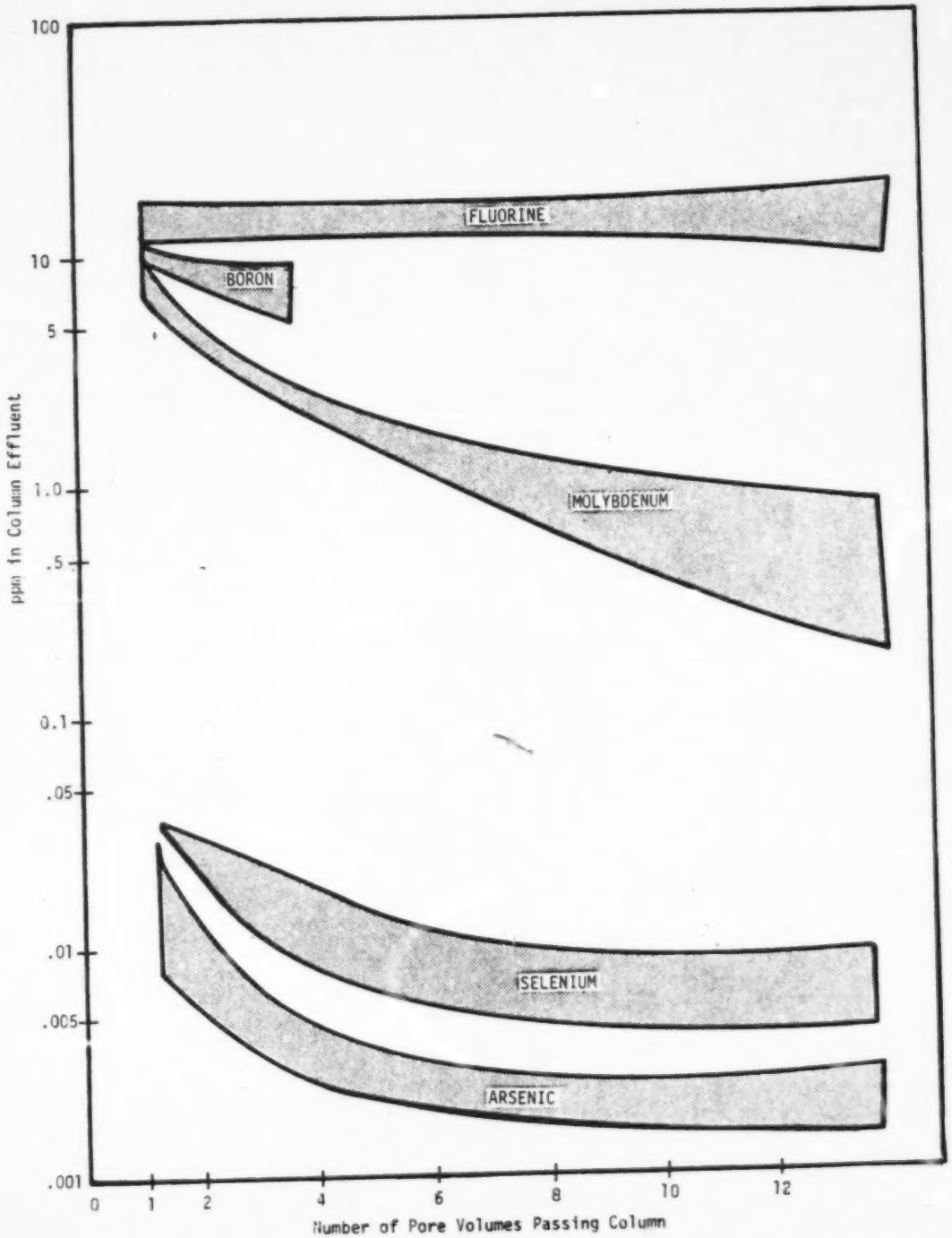

Figure 4. Average Levels of F, B, Mo, As and Se in Leachates from Columns Containing TOSCO II Retorted Shale(38)

TOSCO II shale and maintains a level of about 10 mg/l in leachate for a considerable period of time. In contrast, Mo, As, and Se quickly decrease in concentration in leachates. The data available at present are not sufficient to indicate the rate of boron release from TOSCO II retorted shale.

The Colony Development operation has sponsored studies of runoff and leachates from field test beds of TOSCO II retorted shale (32). The low permeability of compacted TOSCO II shale allows little of the incident rainfall during a storm to penetrate a bed. Water which does penetrate largely rises to the bed surface and is evaporated between rainfall events, leaving surface salt deposits derived from soluble substances in the shale. Runoff can redissolve these deposits and carry suspended and dissolved materials to surface waters. In contrast to rainfall, snowmelt generally occurs at rates slow enough to allow infiltration of most of the meltwater into a TOSCO II shale bed. Infiltrated moisture tends to move as a front into the shale and leachate may appear below shallow portions of a bed (e.g., at the toes of slopes).

Table 17 summarizes measured trace element levels in runoff and leachates from test beds of TOSCO II retorted shale. Concentrations in runoff vary not only with storm duration and intensity, but also with the extent of surface salt deposition which occurs between storms. In general, however, the ranges of measured levels in runoff are similar to those which have been reported for existing surface waters in and around the Federal lease tracts. During natural storms or snowmelt at TOSCO's Rocky Flats, Colorado site, leachate was not produced at the bottom of the test beds. The leachates for which trace element levels are reported in Table 17 represent forced conditions (e.g., continuous water application until leachate is produced). As might be expected from the result of "blender" and "column" experiments, Mo, B, F, As, and Se can be leached from TOSCO shale under saturated flow conditions. In addition, the transition metals Cu, Zn, and Fe are present in initial leachates in concentrations of 0.1 to 3 ppm.

In comparison to existing ground waters on the Federal lease tracts, F and B levels are not unusually high in these leachates. However, Se, As, Cu, Zn, and Fe are present at elevated levels. Although data for Mo in existing groundwaters is not available, it is likely that the leachates also contain significantly larger concentrations of this element.

4.3.3 The Effects of Using Process Water to Moisturize Retorted Shale

The use of process waters to moisturize retorted shales can have two potential effects on the quantities of trace elements which are water soluble. First, additional amounts of some elements are added to shale in water soluble form. Second, dissolved organic and inorganic substances in process waters may affect the solubility of trace elements in the shale.

Table 18 is a comparison of the quantities of selected elements in LERC and TOSCO II retort waters and the water soluble quantities of the same elements in retorted shales. The data in the table suggest that significant additions to the water soluble inventories of Mo, Pb, As, Cu, and Zn, in retorted shale can occur using retort water as the moisturizing agent. Generally, simulated in-situ (LERC) retort waters contain larger total amounts of the listed elements than TOSCO II waters, partly because more water is produced internally in the in-situ gas combustion retort. The comparisons in Table 18 must be qualified by the fact that some trace elements in retort waters exist partly as particulate matter rather than as dissolved substances.

Dissolved organic and inorganic substances in retort waters can potentially increase or decrease the solubility of individual elements in retorted shales. Carboxylic acids, phenols, amines, cyanides, ammonia and other species found in retort waters can form soluble complexes with many metals. The exact effects of such substances in the retorted shale medium is difficult to predict, since both carbonaceous and burned shales partially absorb and immobilize many of the potential metal complexing species. The chemistry of the retorted shale/retort water medium is further complicated by the effects of salinity and alkalinity, and by precipitation reactions which occur. At present the net effect(s) of retort water addition on the water solubility of most trace elements is unknown, since laboratory and field tests to date have not been designed to measure such effects.

Table 17. Levels of Trace Elements Measured in Runoff and Leachates from Field Test Plots of TOSCO II Retorted Shale (ppm)(32)

Element	Runoff from Typical Rain Storms	First Leachate from Sloping Section of Plot	First Leachate from Deepest Portion of Bed	Maximum Levels in Surface Waters/Lease-Tracts C-a	C-b	U-a/U-b	Mean Levels in Ground Waters C-a Alluvial Aquifer	C-a Upper Aquifer	C-a Lower Aquifer	C-b Alluvial Aquifer	C-b Upper Aquifer	C-b Lower Aquifer
Be	-	.0006	-									
Hg	.00002-.00007	.0005	.0003	.001	.0008	.0002	.000	.000	.000	.003	.001	.001
Cd		.006	.003	.003	.006	.004	.03	.002	.001	-	-	-
Sb		.001-.003	.002									
Se	.004-.007	.002 - 2	2	.006	.005	.002	.000	.000	.000	-	-	-
Mo	.03 - .09	3 - 74	5 - 74									
Co	.01	.01	.001-.04									
Ni	.05	.05 -0.2	0.2 - 0.6									
Pb	.009	.004	.003	.009	.011	.005	0.40	.35	.66	.026	.013	.034
As	.005-.008	.02	.08 - .2	.009	.005	.002	.000	.004	.001	.006	.014	.13
Cr	.01 - .07	.004-.009	.004	.08	.02	.01	.000	.005	.000	-	-	-
Cu	.02	.06 - .2	.06 - .2	.008	.010	.013	0.5	.03	.02			
Zr	1001	.001	.003									
B	-	.02 - .9	.02	0.77	0.33	0.09	1.25	0.7	1.8	.7	1.5	3.0
Zn	.01 - .09	1	1 - 3									
Li	.02 - .2	.007-.076	.07 -.8									
V	.003	.003-.006	.004-.1									
Mn	.004	.06 - .2	.06 - .5									
F	.02 - 3	2 - 17	.006- 12	10	1.3	0.3	.37	4.1	14	.97	18	19
Ba	.02 -.04	.06 -.1	0.1	0.40	.20	.14	.003	.000	.000	.09	.10	1.0
Fe	.09 -.6	.6 - 2	1 - 3									

Table 18. Comparison of Water Soluble Trace Element Quantities in Retorted Shale to the Quantities in Retort Waters

Element	Quantity in * Retorted Shale which is Water Soluble (Mg/Kg)	Quantity in* LERC Retort Water Added to Shale (Mg/Kg)	Quantity in* TOSCO II Retort Water Added to Shale (Mg/Kg)
Cd	.04	< .0001	-
Se	.05	< .0005	-
Mo	< .05 - 8	.02	.003
Pb	.003 - .14	.005	.001
As	0.1	0.14	.001
Cr	< .05 - 1.3	.001	.01
Cu	0.01	0.01	< .0001
B	1 - 12	0.14	< .0001
Zn	.02 - .12	.02	.01
F	20-80	1.1	.001

* Data from Table 16
** Data from Table 11, assumes 45 liters of retort water produced per ton of raw shale
***Data from Table 11, assumes 10 liters of retort water produced per ton of raw shale.

4.3.4 The Accumulation of Trace Elements by Vegetation Growing on Retorted Shale

The water solubility of specific trace elements in retorted shales suggests that they may be available to vegetation growing on such shales. The concern with trace element accumulation stems for both toxicity to plants (e.g., B) and to herbivores (e.g., F, As, Mo, Se).

In 1973, revegetation test plots of TOSCO II and USBM retorted shales were established at Parachute Creek (Colony property) and at Anvil Points. In August of 1974, barley plants growing on shales at the Parachute Creek site were sampled and analyzed for selected trace elements (Mn, Fe, Cu, Zn, Sr, Zn, Mo, and Cd). Compared to a soil control, only molybdenum appeared to be higher in barley growing on both retorted shales (42). Zn concentrations also were higher in plants from the TOSCO II plot than in plants from native soils.

During 1976, samples of wastern wheatgrass and four wing salt bush were obtained from these plots and analyzed for B, F, As, Mo, and Se (41). Table 19 presents the typical analytical results for the above ground portions of these plants based on dry weight of vegetation. Levels of molybdenum and boron appear higher in wheatgrass grown on TOSCO II shale than on native soils. A similar trend is not as apparent for USBM retorted shale. Molybdenum also appears to be present at elevated levels in four wing salt bush grown in USBM shale, at least at the Parachute Creek site. Fluorine levels in wheatgrass do not show a strong trend for the retorted shale media compared to native soils.

The data for arsenic are not adequate to establish a trend, since a true profile of native soil was not used as a control. Selenium data were not available at the time of this writing. Samples of vegetation were taken from both north and south facing slopes, and the results show no obvious trends within the accuracy and reproducibility of the analyses.

These studies suggest that available boron in retorted shales may exceed the threshold of toxicity for sensitive plants and that certain fluora may accumulate levels of molybdenum toxic to herbivors. For instance, many common fruit trees exhibit symptoms of boron toxicity at 2 ppm levels (dry folige basis). Domestic livestock begin to show symptoms of molybdenosis on a diet of vegetation containing 15-20 ppm Mo (low copper levels and high sulfate sulfur levels are also involved in molybdenosis).

Table 19. Trace Element Levels in Vegetation Grown on Retorted Shales (41)
(ppm dry weight plant material basis)

Location/Growth Medium	Western Wheatgrass				Four Wing Salt Bush
	Boron	Fluoride	Arsenic	Molybdenum	Molybdenum
Parachute Creek					
Natural soils	25	2	0.12*	0.8	6
TOSCO II retorted shale	100	3	0.2	3	7
USBM retorted shale	14-93	3.5	0.3	3	27
Anvil Points					
Natural soils	19-115	2.4	-	3	3
TOSCO II retorted shale	200	5		5	2
USBM retorted shale	40-70	4		4	6

*Natural soil (12") over TOSCO II retorted shale, similar levels found in wheatgrass grown on 24" natural soil over USBM retorted shale

4.4.2 Upgrading and Refining

On site upgrading or refining of crude shale oil planned for the first generation of commercial operations consists of 1) filtration for solids removal, 2) distillation and coking, and/or 3) catalytic hydrogeneration of whole shale oil or its fractions. Filtration (e.g., dicitomateous earth) will generally remove insoluble inorganic materials and the trace element components of such materials. As was discussed previously, however, only a portion of the trace element levels in shale oil can be attributed to the presence of raw or retorted shale fines.

In the distillation of shale oil, most minor elements tend to concentrate in the higher boiling fractions and in shale coke. Table 18 presents data for the As, Ni, V, and Fe contents of TOSCO II and Paraho Direct Mode shale oil fractions. Although the fraction analyses for Paraho oil are not entirely consistent with whole oil analyses, the data show the trend toward higher levels of Ni, V, and Fe in higher boiling fractions. In contrast, arsenic is apparently distributed throughout the boiling range.

In a commercial operation, elements such as Ni, V, Fe will tend to concentrate along with shale fines in coke. Assuming that about 10% of whole shale oil becomes coke during upgrading, a typical shale coke analysis might be approximated by multiplying the values for non-volatile elements in Table 7 for crude shale oil by ten. Volatile elements (As and probably Se, Hg, and Sb) are likely to be found in lower boiling fractions at levels in the same range as in whole shale oil.

Hydrotreating of shale oil for sulfur and nitrogen removal is typically performed over nickel or cobalt molybdate catalyst supported on alumina. Many metallic and heavy elements are known to decrease the activity of these and similar catalysts. The levels of most elements which are encountered in shale oils are generally similar to or less than those for many petroleum crudes. Further, techniques have been developed in the petroleum industry to avoid excessive catalyst deterioration due to the presence of certain trace elements. The relatively high arsenic levels in shale oils have necessitated steps for its removal to maintain bulk catalytic activity during hydrotreating operations. The steps generally employ a selective absorbant for As (and other trace elements) or a portion of the catalyst bed itself as the removal media. The contaminated media would be periodically removed for disposal or reprocessing.

Table 19. As, Ni, V, and Fe Distribution in Shale Oil Distillation Fractions (27,25) (ppm by weight)

Boiling Range	Shale Oil/Element				
	TOSCO II As	Paraho As	Paraho Ni	Paraho V	Paraho Fe
IBP - 200°C	10	-	1.9	<.02	7
200°- 480°C	52	-	0.3	<.02	8
400°C +	38	-	1.5	0.1	36
Whole Shale Oil	40	20	2.5	0.37	71

For Ni - Mo catalyst on alumina, 7% by weight of As would be the approximate cutoff point for replacement, since at greater percentages As begins to appear in the hydrotreated product. Spent catalyst would also contain around 10% carbon, 8% sulfur and small quantities of other shale derived elements (Sb, Se, and transition metals) (27,39). The chemical form(s) of arsenic on spent catalyst is not known, although As_2S_3 or elemental As are likely candidates.

Spent catalyst would generally be disposed of with other solid wastes in a commercial oil shale operation until sufficient quantities of such materials could justify shipping to a preprocessor. In recent years, prices for metals such as Ni, Co, and Mo have increased to the point where reclaimation firms can offer attractive terms to refiners for spent catalysts (40). However, contaminants such as arsenic in spent catalysts from shale operations may present technical, economic, or waste disposal problems for reclaimers. Thus, direct disposal with other wastes is the likely fate of these materials, at least during the early stages of oil shale development. The quantities requiring disposal is small relative to the quantities of retorted shale and catalyst materials may be placed in steel drums for landfill disposal as is a common practice with spent petroleum catalysts, or mixed with retorted shale and spread over a larger area in a disposal pile. At this time there is little information to indicate the chemical stability or potential for mobility of catalyst metals (Ni, Co, Mo) and trace element contaminants (As, Se, Hg) disposed in either concentrated or dispersed form with retorted shale.

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